



One/two-photon cationic polymerization in visible and near infrared ranges using two-branched sulfonium salts as efficient photoacid generators



Xingyu Wu^a, Ming Jin^{a,*}, Jianchao Xie^a, Jean Pierre Malval^b, Decheng Wan^a

^a School of Materials Science and Engineering, Tongji University, 4800 Caoan Road, Shanghai, 201804, PR China

^b Institute de Science des Matériaux de Mulhouse, UMR CNRS 7361, Université de Haute-Alsace, 15 Rue Jean Starcky, Mulhouse, 68057, France

ARTICLE INFO

Article history:

Received 11 May 2016

Received in revised form

13 June 2016

Accepted 14 June 2016

Available online 16 June 2016

Keywords:

Two-photon absorption

Cationic polymerization

Sulfonium salts

Photoacid generators

ABSTRACT

This paper describes the synthesis and photochemical behavior of two two-branched sulfonium-based photoacid generators (PAGs). The branched structure influences the optical properties of the PAGs by increasing absorption wavelengths and molar extinction coefficients as well as enhancing acid production under one/two-photon irradiation. The two-branched structures collectively showed twofold higher H⁺ production abilities and improved two-photon absorption cross-sections compared with those in the corresponding mono-branched PAGs. Photochemical mechanisms were investigated through UV–Vis spectra analysis, molecular orbital calculations, and fluorescence analysis. These novel two-branched D- π -A type sulfonium-based photoinitiating systems are efficient cationic photoinitiators (epoxide conversion = 70%–85% and vinyl conversion > 75%) even under conditions with low initiator concentration (1 wt%) and curing light intensities (5 mW cm⁻²) upon exposure to visible light-emitting diodes (e.g., 405 nm). These two-photon fabricated microstructures also exhibit potential as cationic two-photon initiators.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Two-photon absorption (2 PA) is a nonlinear optical process that involves simultaneous absorption of two photons of identical or different frequencies and leads to excitation of a molecule from the ground state to the excited state [1]. 2 PA-related processes, such as nonlinear transmission and quadratically intensity-dependent properties, are utilized in optoelectronic devices, including 3D optical data storage systems [2]. The process can also be adopted in triggering subsequent events, such as fluorescence or chemical reactions [3,4] in biological imaging, photodynamic therapy [5], and 3D photolithography [6–9]. In the last two decades, 2 PA cross-sections (δ) for organic 2 PA chromophores have been considerably improved. To maximize the δ of chromophores, researchers have developed various strategies, including extension of conjugation length and dimensionality [10] as well as introduction of electron donating/accepting groups to create “push–pull” systems [11]. For example, symmetrically substituted D- π -D and D- π -A- π -D

chromophores are effective designs for increasing δ [12].

Photoacid generators (PAGs) constitute an important class of cationic photoinitiators and can be strategically used in the field of photoresists [13–15]. Applications of PAGs have been extensively developed in various research domains, such as microelectronics, photosensitized resins, and 3D microfabrication [16–21]. Considering the advantages of PAGs, scholars have become increasingly interested in designing new PAGs that can be excited with long-wavelength light by two-photon modes [18,22–24]. Perry et al. [25] fabricated a sulfonium-based PAG by introducing a bis [(diarylamino)styryl] benzene derivative; the products exhibited high quantum yield for acid generation ($\Phi_{\text{H}^+} \sim 0.5$) and a large 2 PA cross-section (δ) ($\delta_{\text{max}} = 690 \text{ GM}$). In this substance, the sulfonium salt groups were symmetrically associated with one benzene ring of the arylamino moieties. Belfield et al. [18] developed a 1,8-bis(4'-styryl) fluorene with two *para*-substituted diphenyl-sulfonium groups at both extremities of the PAGs. In our previous studies, we investigated two materials, namely, 4-ethoxystilbene [3] or 4-*N,N*-diphenylaminostilbene [24,26,27], whose strong electron-donating group and elongated D- π -A conjugation red shifted the absorbance of PAGs and enlarged the 2 PA cross-section to ca. 600 GM.

Although several new photoinitiators have been developed for

* Corresponding author.

E-mail address: mingjin@tongji.edu.cn (M. Jin).

the photopolymerization under various LEDs [28–33], developing novel PAGs sensitive to two-photon excitation is an essential step toward promising applications. The multibranch strategy is a relevant tool used to modulate linear and nonlinear absorption properties without drastic effects on the energy position of electronic transitions [34–36]. The para-to-meta substitution strategy is also an effective technique used to adjust the absorption wavelength and influence photolysis efficiency in sulfonium salt PAGs [24].

In this study, we designed and prepared four two-branched D- π -A typed sulfonium-based PAGs (Bi-Para and Bi-Meta; Scheme 1). These PAGs maintain an excellent transparency in a large portion of the visible and near-infrared regions and are thus suitable for one/two-photon polymerization. The fabricated PAGs could be a potential cationic one/two-photon photoinitiator, given their outstanding efficiency or acid generation ability.

2. Experimental section

2.1. Materials

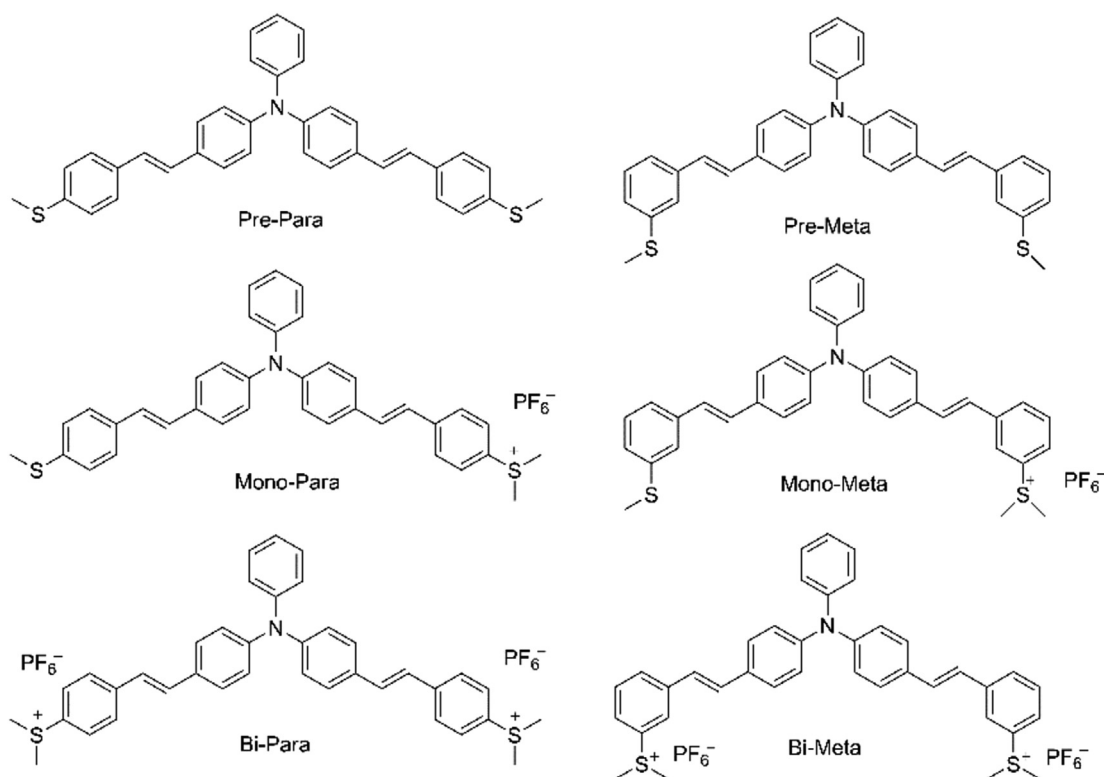
All the chemicals used for synthesis were purchased from Sinopharm Chemical Reagent Co., Ltd., TCI, Alfa Aesar, or J&K Chemical. The reagents were utilized without further purification unless otherwise specified. All the solvents employed for photo-physical measurements were Fluka spectroscopic grade. The monomer cyclohexene oxide (CHO, 98%) and triethyleneglycol divinyl ether (DVE-3, 98%) were purchased from Sigma-Aldrich from the highest purity available and used as received without further purification.

2.2. General instrumentations

Proton and carbon nuclear magnetic resonance spectra (^1H , ^{13}C NMR) were recorded on a Bruker Avance 400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from the Me_4Si resonance, which was used as the internal standard when recording NMR spectra. Mass spectra were obtained on a Micromass GCTM. The molecular weights of the photopolymers were determined using a GPC instrument equipped with MZ-Gel SD plus columns (HR series 3, 4, and 5E), with THF as eluent at a flow rate of 1 mL min^{-1} and a Waters 410 differential refractometer detector. The melting point of molecules were determined using Melting Point Apparatus (Nikon-Ti, Co. Ltd. Japan). IR data of molecules were measured with a Thermo-Nicolet iS5 instrument infrared spectrometer.

UV–Vis spectra were recorded on a Mapada UV-6300 spectrophotometer. The photodecomposition process in a solution of acetonitrile and CHO were monitored by UV–Vis spectra under a light-emitting diode (LED) point curing (Uvata, Shanghai). irradiation of 405 nm (0.4 mW cm^{-2}). Steady-state fluorescence spectra are collected from a Hitachi-2700 spectrofluorometer. Emission spectra are spectrally corrected, and fluorescence quantum yields include the correction due to solvent refractive index are determined relative to quinine bisulfate in 0.05 M sulfuric acid ($\Phi_{\text{fl}} = 0.52$) [3].

Quantum yields for acid generation were measured under irradiation at 405 nm LED. All irradiated PAGs dissolved in acetonitrile were previously N_2 degassed. The progress of the photoreaction was monitored via UV–Vis absorption spectroscopy. The absorbance at the excitation wavelength must be higher than 2.5 before assuming a total absorption of the incident photons. The dose rates were maintained sufficiently small such that the changes in absorbance were lower than 10%. Rhodamine B (RhB) was used as



Scheme 1. Molecular structures of the precursor and PAGs.

Download English Version:

<https://daneshyari.com/en/article/175404>

Download Persian Version:

<https://daneshyari.com/article/175404>

[Daneshyari.com](https://daneshyari.com)